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# Photoactivation of Molecular Oxygen by an Iron(III) Porphyrin with Mg-Al Layered Double Hydroxide for Aerobic Epoxidation of Cyclohexene

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The photocatalytic aerobic epoxidation of cyclohexene proceeded under visible light irradiation only when 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin iron(III) chloride ($Fe^{III}$(TPFPP)Cl) was combined with Mg-Al layered double hydroxide (Mg-Al LDH) as a solid base in chloroform. The OH groups in the Mg-Al LDH exchanged with the axial Cl ligands in $Fe^{III}$(TPFPP)Cl to afford $Fe^{III}$(TPFPP)OH, which functioned photocatalytically in the presence of Mg-Al LDH, but was inactive in its absence. The band in the action spectrum agreed well with the Soret band in the UV-vis absorption spectrum of $Fe^{III}$(TPFPP)OH. The spectral changes indicated the reduction of $Fe^{III}$(TPFPP)OH to $Fe^{II}$(TPFPP) under visible light irradiation, which in turn activates $O_2$ which could be used for the epoxidation of cyclohexene.

## Introduction

Molecular oxygen is an important oxidizing agent, but because it is very difficult to activate at ambient temperature and pressure, studies on selective oxidation by $O_2$ have rarely been reported. However, there are promising photocatalytic systems that can be used for environmentally friendly and selective oxidation by $O_2$. Many research groups have focused on methods to activate $O_2$, although the resulting photocatalytic activities remain insufficient.[1] Recently, a number of reports have described extensive investigations of photocatalytic selective oxidation using an organic complex (photosensitizer) immobilized on a solid or organic–inorganic hybrid material. Yamashita et al.[2] found that tris(2-2′-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+}$) complexes contained in a series of Y-type zeolite cages with various extra-framework alkali metal cations exhibited photocatalytic activity for the selective oxidation of styrene and α-methyl styrene. Y-type zeolites with lighter alkali metal cations acted as more efficient hosts than those containing heavier alkali metal cations for the acceleration of photocatalytic epoxidation. Shiragami et al.[3] reported that the silica gel-supported hydroxo(tetraphenylporphyrinato)antimony(V) complex, $[SbTPP(OH)]^+/SiO_2$, exhibited good activity for the photocatalytic oxidation of cyclohexene under visible light irradiation. Maldotti et al. reported photocatalytic aerobic oxidation using porphyrin complexes[4] and/or a polyoxometalate[5] under UV light irradiation. In their study, an $Fe^{III}$(TPFPP)Cl/Nafion system in ethanol or 2-propanol exhibited good activity for the selective photooxidation of cyclochexene under UV light irradiation (330–400 nm).[6] The main product was *trans*-cyclohexane-1,2-diol monoethyl ether, and allylic oxidation products (2-cyclohexen-1-ol and 2-cyclohexen-1-one) were formed in very minor amounts. Hence, they suggested that the reaction proceeds through the formation of 1,2-epoxycyclohexane, which undergoes nucleophilic attack by the alcohol solvent under acid conditions.

We have investigated an environmentally friendly CO photooxidation[7] as well as the selective photocatalytic oxidation of alkanes[8], olefins[9], and alcohols[9d] in the gas phase and various hydrocarbons in the liquid phase,[10] using an orthovanadate ($(V=O)O_3$)-like species (i.e., a vanadium oxo complex) dispersed on various solid materials (e.g., $SiO_2$ and $Al_2O_3$).[11] We also determined that the selective photocatalytic oxidation of alcohols[12] and amines[13] in the presence of $O_2$ takes place over niobium oxide ($Nb_2O_5$) under visible light irradiation. The photoactivation mechanism for the reaction of alcohol over $Nb_2O_5$ is different from the typical electron transfer mechanism on semiconductor photocatalysts: the alkoxide species adsorbed on $Nb_2O_5$ is activated, transferring an electron to the conduction band to reduce $Nb^{5+}$ to $Nb^{4+}$, and leaving a hole in the alkoxide.[12c, 13b]

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In our previous communication, we reported the photocatalytic aerobic oxidation of cyclohexene in the presence of 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin iron(III) chloride ($Fe^{III}$(TPFPP)Cl) and various solid metal oxides, and found that a solid base was necessary to obtain epoxy compounds.[14] Solid bases such as MgO, CaO, and ZnO enhanced the conversion of cyclohexene to 1,2-epoxycyclohexane with high selectivity, while amphoteric metal oxides such as $Al_2O_3$, $ZrO_2$, and $TiO_2$ showed moderate additive effects. However, inert materials such as $SiO_2$ and solid acids like $Ta_2O_5$, $Nb_2O_5$, and $WO_3$ did not enhance photocatalytic activity. Using a solid base catalyst such as Mg-Al layered double hydroxide (Mg-Al LDH), the maximum conversion of cyclohexene to 1,2-epoxycyclohexane could be achieved with high selectivity. The $Fe^{III}$(TPFPP)Cl/Mg-Al LDH system functions as an effective photocatalyst for the aerobic epoxidation of alkenes under visible light irradiation, although $Fe^{III}$(TPFPP)Cl is not immobilized on the Mg-Al LDH. Our results reveal that solid bases, particularly Mg-Al LDH, enhance selectivity for 1,2-epoxycyclohexane in the photocatalytic aerobic epoxidation of cyclohexene. The $Fe^{III}$(TPFPP)Cl/Mg-Al LDH system can be used for the effective epoxidation of various alkenes under visible light irradiation, although "free-base porphyrins" can be used as photosensitizers in allylic oxidation. In this study, we attempted to identify the active species in the photocatalytic epoxidation process under visible light irradiation using the $Fe^{III}$(TPFPP)Cl/Mg-Al LDH system and cyclohexene.

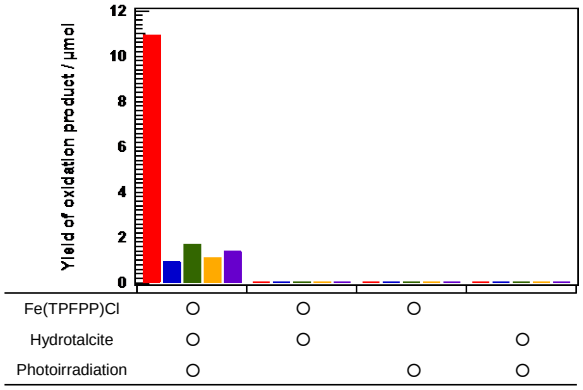


Figure 1. Yields of oxidation products obtained in the photocatalytic aerobic oxidation of cyclohexene in the presence or absence of $Fe^{III}$(TPFPP)Cl and Mg-Al LDH under various conditions after 8 h irradiation: 1,2-epoxycyclohexane (red), 2-cyclohexen-1-ol (blue), 2-cyclohexen-1-one (green), cyclohexanol (yellow), and cyclohexanone (purple). Conditions: $Fe^{III}$(TPFPP)Cl: 5.0 × $10^{-2}$ mM; cyclohexene: 12.5 mM; Mg-Al LDH: 100 mg; solvent: chloroform; and volume: 4 mL.

## Results and Discussion

Figure 1 illustrates the yields of the oxidation products obtained in the photocatalytic aerobic oxidation of cyclohexene with and without $Fe^{III}$(TPFPP)Cl, Mg-Al LDH, and visible light irradiation after 8 h (as control experiments). In the presence of $Fe^{III}$(TPFPP)Cl and Mg-Al LDH under visible light irradiation, 1,2-epoxycyclohexane was obtained as the main product, while 2-cyclohexen-1-ol, 2-cyclohexen-1-one, cyclohexanol, and cyclohexanone were generated as by-products. These products were hardly formed in the absence of photoirradiation, $Fe^{III}$(TPFPP)Cl, or Mg-Al LDH, indicating that the Fe-porphyrin complex works photocatalytically in cooperation with Mg-Al LDH. Figure 2 shows the time course of the formation of 1,2-epoxycyclohexane in the presence of (a) $O_2$ and (b) Ar. The photocatalytic epoxidation promoted by the $Fe^{III}$(TPFPP)Cl/Mg-Al LDH system hardly proceeds in the absence of $O_2$, but the rate of 1,2-epoxycyclohexane formation is dramatically enhanced in its presence. The amount of 1,2-epoxycyclohexane evolved in the presence of $O_2$ (11.0 μmol) was ten times that in the presence of Ar (1.14 μmol) after 8 h irradiation. This strongly indicates that molecular $O_2$, activated by the $Fe^{III}$(TPFPP)Cl/Mg-Al LDH system, plays a major role in the photocatalytic aerobic epoxidation of cyclohexene. Hence, it can be concluded that both $Fe^{III}$(TPFPP)Cl as a homogeneous catalyst and the solid base Mg-Al LDH as a promoter contribute to this photocatalytic process and activate molecular $O_2$ via a visible light response.

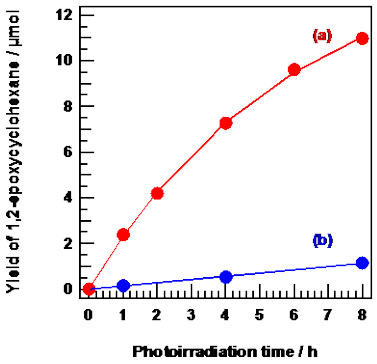


Figure 2. Time course of the formation of 1,2-epoxycyclohexane obtained in the photocatalytic reaction of cyclohexene in the presence of (a) $O_2$ and (b) Ar after 8 h irradiation. Conditions: $Fe^{III}$(TPFPP)Cl: 5.0 × $10^{-2}$ mM; cyclohexene: 12.5 mM; Mg-Al LDH: 100 mg; solvent: chloroform; and volume: 4 mL.

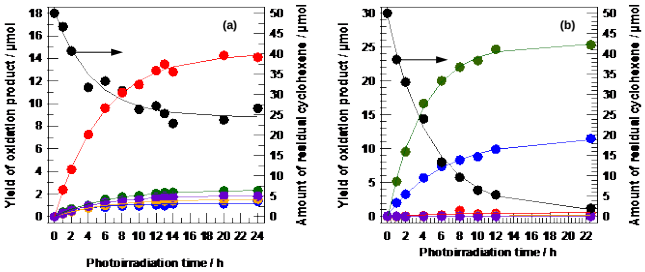


Figure 3. Time courses of the oxidation products formation and cyclohexene consumption during photocatalytic aerobic oxidation (a) in the $Fe^{III}$(TPFPP)Cl/Mg-Al LDH/chloroform system and (b) in the $H_2$TPFPP/Mg-Al LDH/chloroform system under the optimized conditions: cyclohexene (black), 1,2-epoxycyclohexane (red), 2-cyclohexen-1-ol (blue), 2-cyclohexen-1-one (green), cyclohexanol (yellow), and cyclohexanone (purple). Conditions: $Fe^{III}$(TPFPP)Cl or $H_2$TPFPP: 5.0 × $10^{-2}$ mM; cyclohexene: 12.5 mM; Mg-Al LDH: 100 mg; solvent: chloroform; and volume: 4 mL.

Figure 3 shows the time courses of the formation of the oxidation products and the decrease in the cyclohexene substrate during the photocatalytic aerobic oxidations using (a) $Fe^{III}$(TPFPP)Cl and (b) $H_2$TPFPP with Mg-Al LDH under the optimized conditions. In the presence of $Fe^{III}$(TPFPP)Cl, the main 1,2-epoxycyclohexane product was formed at an initial rate of 2.35 μmol $h^{-1}$. In addition, minor amounts of 2-cyclohexen-1-ol, 2-cyclohexene-1-one, cyclohexanol, and cyclohexanone were generated (Figure 3(a)). The carbon balance was clearly maintained after 8 h photoirradiation (Figure S1, Supplementary Information (SI)). In the liquid phase, the amount of cyclohexene as a substrate was detected to 31.4 μmol, and oxidation products were generated in the following quantities: 1,2-epoxycyclohexane, 8.86 μmol; 2-cyclohexen-1-ol, 0.87 μmol; 2-cyclohexene-1-one, 1.39 μmol; cyclohexanol, 1.21 μmol; and cyclohexanone, 1.50

μmol. Additionally, we observed 26.2 μmol $CO_2$ in the gas phase; however, the amount of cyclohexene consumed for the formation of $CO_2$ (4.37 μmol) is half higher than that for the formation of 1,2-epoxycyclohexane (8.86 μmol). The cyclohexene conversion and selectivity for 1,2-epoxycyclohexane after 20 h photoirradiation were 52.4% and 54.5%, respectively. The turnover number (TON) of cyclohexene, defined as the amount of products after 20 h (26.2 μmol) normalized to the addition of $Fe^{III}$(TPFPP)Cl (0.2 μmol), reached 131. On the other hand, when the free-base porphyrin ($H_2$TPFPP) was used as catalyst, only the allylic oxidation products 2-cyclohexen-1-ol and 2-cyclohexen-1-one were obtained (Figure 3(b)). $H_2$TPFPP is generally known to act as a photosensitizer under visible light irradiation to generate singlet oxygen species.[15] Singlet oxygen can easily abstract an allylic hydrogen atom. Since the epoxidation of cyclohexene proceeds preferentially in our photocatalytic $Fe^{III}$(TPFPP)Cl/Mg-Al LDH system, it is apparent that the main active $O_2$ species involved in the reaction is not singlet oxygen and that the mechanism of 1,2-epoxycyclohexane formation is different from that of the allylic oxidation products.

The amounts of oxidation products increased with the photoirradiation time, and were inversely correlated with the cyclohexene concentration in Figure 3(a). The product quantities and cyclohexene consumption rate were virtually constant after 20 h because of the competitive decomposition of $Fe^{III}$(TPFPP)Cl. The porphyrin catalyst was not detected by UV-vis spectroscopy in the solution after 24 h reaction. The time course for the consumption of $Fe^{III}$(TPFPP)Cl, estimated from the reduction of the Soret band in the UV-vis absorption spectra, was consistent with that for the formation of 1,2-epoxycyclohexane, indicating that the rate of epoxide formation depends on the concentration of $Fe^{III}$(TPFPP)Cl (Figure S2, SI). Even after the porphyrin complex was completely consumed, oxidation could be resumed by the addition of fresh $Fe^{III}$(TPFPP)Cl to the reaction mixture (Figure 4). In this case, the concentration of $Fe^{III}$(TPFPP)Cl was $1.0 \times 10^{-2}$ mM. After 8 h, the amount of 1,2-epoxycyclohexane remained virtually constant and no $Fe^{III}$(TPFPP)Cl was detected in the solution by UV-vis spectroscopy, indicating its complete decomposition. The epoxide yields after the second and third additions of catalyst were more or less same as the yield obtained after the first addition. This showed that the decomposition of $Fe^{III}$(TPFPP)Cl competed with the formation of 1,2-epoxycyclohexane.

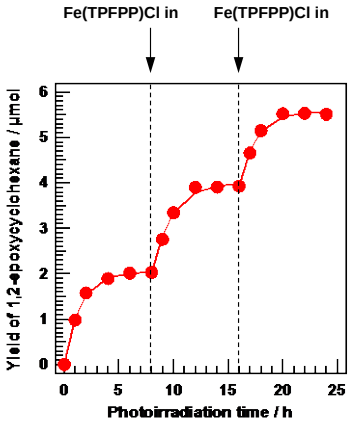


Figure 4. Dependence of adding of $Fe^{III}$(TPFPP)Cl on the formation of 1,2-epoxycyclohexane in the photocatalytic aerobic oxidation of cyclohexene in the $Fe^{III}$(TPFPP)Cl/Mg-Al LDH/chloroform system. Conditions: $Fe^{III}$(TPFPP)Cl: $1.0 \times 10^{-2}$ mM; cyclohexene: 12.5 mM; Mg-Al LDH: 100 mg; solvent: chloroform; volume: 4 mL.

The photocatalytic aerobic epoxidation of cyclohexene does not proceed without Mg-Al LDH, as shown in Figure 1. The Fe-porphyrin complex and the Mg-Al LDH function cooperatively in the oxidative transformation under visible light irradiation. Figure 5 shows the time courses of the formation of 1,2-epoxycyclohexane and the consumption of the substrate during photocatalytic aerobic oxidation with the $Fe^{III}$(TPFPP)Cl/Mg-Al LDH system when (a) Mg-Al LDH was removed after 4 h and (b) of Mg-Al LDH was added after 4 h. In both cases, the epoxide was generated only in the presence of Mg-Al LDH, and none was produced in its absence.

After the photocatalytic aerobic oxidation, the solid base was examined by filtering the suspension to recover the Mg-Al LDH. The Mg-Al LDH was thoroughly washed with methanol, followed by dissolution in aqueous $H_2SO_4$ solution (10%). The resultant solution became cloudy upon titration with aqueous $AgNO_3$, indicating the formation of AgCl (Figure S3, SI). Hence, it is likely that chloride ions are retained in the Mg-Al LDH after the reaction. A suspension of Mg-Al LDH and chloroform without $Fe^{III}$(TPFPP)Cl was irradiated, filtered, washed, redissolved, and titrated. However, this sample did not become cloudy upon titration with aqueous $AgNO_3$. Actually, the photocatalytic activity was dependent on amount of Mg-Al LDH introduced. The amount of 1,2-epoxycyclohexane evolved gradually increased with increasing of amount of Mg-Al LDH introduced up until 100 mg and then was saturated (Figure S4, SI). Accordingly, the chloride ion must be derived not from chloroform but from $Fe^{III}$(TPFPP)Cl. We have confirmed that $Fe^{III}$(TPFPP)Cl is not adsorbed on Mg-Al LDH; therefore, the axial Cl ligand in $Fe^{III}$(TPFPP)Cl moves to the Mg-Al LDH surface.

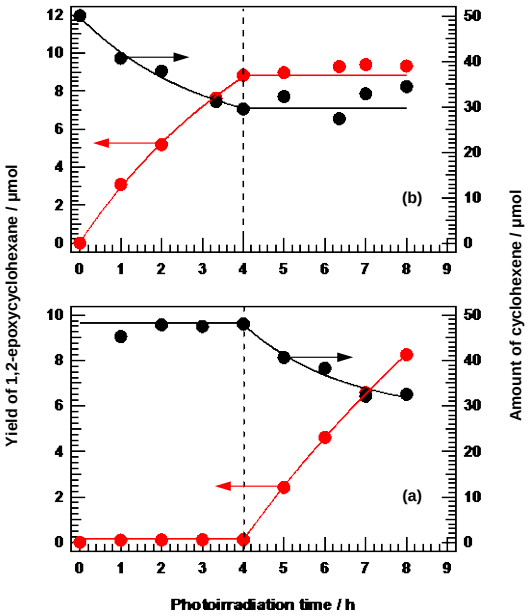


Figure 5. Time courses of 1,2-epoxycyclohexane formation (red) and cyclohexene consumption (black) in the photocatalytic aerobic oxidation of cyclohexene in the $Fe^{III}$(TPFPP)Cl/Mg-Al LDH/chloroform system in the case of (a) removal of Mg-Al LDH after 4 h and (b) addition of Mg-Al LDH after 4 h. Conditions: $Fe^{III}$(TPFPP)Cl: $5.0 \times 10^{-2}$ mM; cyclohexene: 12.5 mM; Mg-Al LDH: 100 mg; solvent: chloroform; volume: 4 mL.

Figures 6 presents the UV-vis absorption spectra of $Fe^{III}$(TPFPP)Cl before and after the addition of Mg-Al LDH and NaOH. As is seen in Figure 6(a), a typical Soret band appears at 410 nm, and two Q-bands are observed at 567 and 629 nm. After

the addition of Mg-Al LDH, the Soret band is blue-shifted to 406 nm, and only one Q band appears at 564 nm (Figure 6(b)). Agarwala et al.[16] reported that $Fe^{III}$(TPFPP)Cl is converted to $Fe^{III}$(TPFPP)OH in acetonitrile in the presence of water. Their reported UV-vis spectrum is similar to that in Figure 6(b). $Fe^{III}$(TPFPP)OH was synthesized by the following method. $Fe^{III}$(TPFPP)Cl was mixed with aqueous NaOH at room temperature for 1 h, and then the resulting solution was extracted with chloroform. The UV-vis absorption spectrum of the solution is consistent with that of $Fe^{III}$(TPFPP)OH reported by Agarwala et al.[16] (Figure 6(c)). It was concluded that the axial Cl ligands in $Fe^{III}$(TPFPP)Cl are exchanged with the OH groups in Mg-Al LDH.

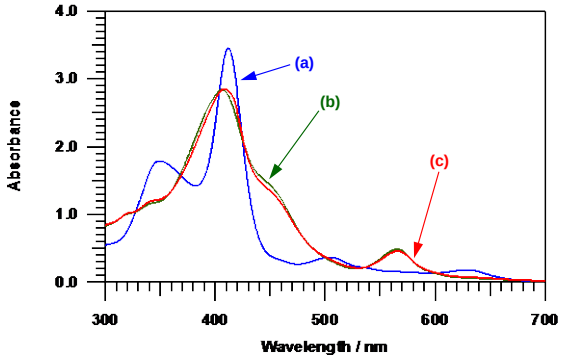


Figure 6. UV-vis absorption spectra of $Fe^{III}$(TPFPP)Cl (a) before (blue) and (b) after (green) the addition of Mg-Al LDH and (c) with an aqueous NaOH solution (red).

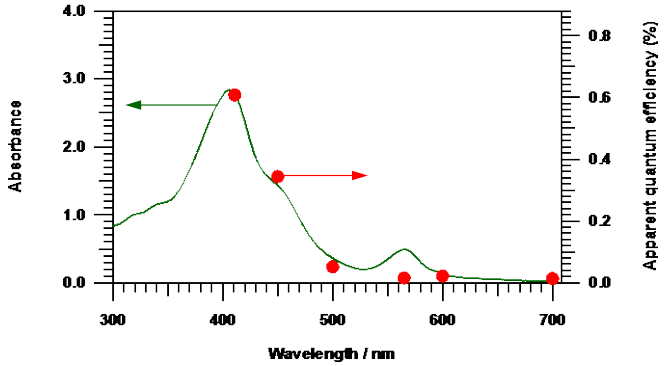


Figure 7. UV-vis absorption spectra of $Fe^{III}$(TPFPP)Cl after the addition of Mg-Al LDH (green), and apparent quantum efficiency for the photocatalytic aerobic oxidation of cyclohexene as a function of the wavelength of incident light (red circle).

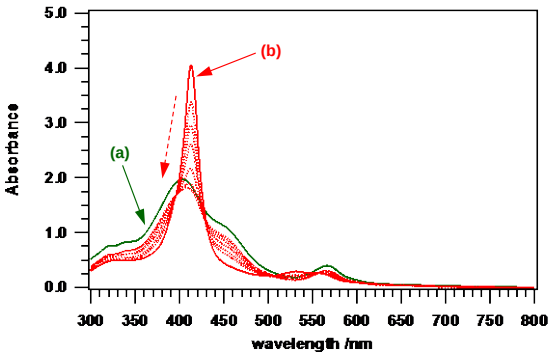


Figure 8. UV-vis absorption spectra of $Fe^{III}$(TPFPP)Cl with Mg-Al LDH (a) after degassing by the freeze-pump-thaw method and (b) after 10 min visible light irradiation. The dashed spectra show the changes in Figure 8(b) in the dark between 10 and 270 min.

Figure 7 shows the apparent quantum efficiency for the photocatalytic aerobic oxidation of cyclohexene as a function of the wavelength of incident light (action spectrum). The band in the action spectrum is in good agreement with the Soret band in the UV-vis absorption spectrum of $Fe^{III}$(TPFPP)OH (Figure 6(b)). Accordingly, the charge separation of the Soret band contributes to the rate of photocatalytic aerobic epoxidation of cyclohexene under visible light irradiation. Although we carried out the cyclohexene oxidation using $Fe^{III}$(TPFPP)OH alone, only a tiny amount of 1,2-epoxycyclohexane was observed. It was not surprising that the epoxide was also generated immediately upon the introduction of Mg-Al LDH into the $Fe^{III}$(TPFPP)OH solution. Therefore, we conclude that solid bases such as Mg-Al LDH not only facilitate ligand exchange with $Fe^{III}$(TPFPP)OH, but also act as promoters in the presence of $Fe^{III}$(TPFPP)OH for the photocatalytic aerobic epoxidation of cyclohexene.

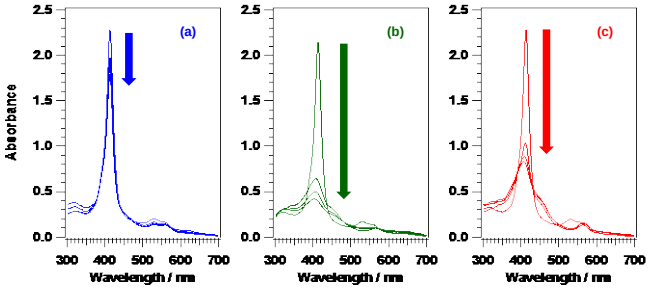


Figure 9. Decrease in the Soret band of $Fe^{II}$(TPFPP) in the presence of $O_2$ (a) in the dark, (b) under visible light irradiation, and (c) under visible light irradiation together with cyclohexene.

As mentioned above, $Fe^{III}$(TPFPP)OH rather than $Fe^{III}$(TPFPP)Cl is activated under visible light irradiation. Figure 8 shows the UV-vis absorption spectra of $Fe^{III}$(TPFPP)Cl with Mg-Al LDH after degassing with the freeze-pump-thaw method followed by visible light irradiation. The UV-vis absorption spectrum after 10 min irradiation (Figure 8(b)) was different from that prior to irradiation (Figure 8(a)). The Soret band at 406 nm was shifted to 413 nm and the absorbance increased in intensity after photoirradiation. The UV-vis absorption spectrum after 10 min visible light irradiation was gradually restored to the original UV-vis absorption spectrum of $Fe^{III}$(TPFPP)OH in the dark with isosbestic points; however, the absorbance of the restored UV-vis absorption spectrum was not perfectly consistent with that of the original spectrum because a small amount of $Fe^{III}$(TPFPP)OH was decomposed under irradiation. Bartocci et al.[17] reported that the reversible peak change is comparable to the redox reaction between Fe(III) and Fe(II) in the case of iron(III) meso-tetrakis(2,2-dichlorophenyl)porphyrin (Fe(TDCPP)) under photoirradiation ($\lambda$ > 350 nm). Actually, the UV-vis absorption spectrum of $Fe^{III}$(TPFPP)OH reduced by $Na_2S_2O_4$ was almost consistent with that after visible light irradiation (Figure S5, SI). We concluded that $Fe^{III}$(TPFPP)OH, which is generated from $Fe^{III}$(TPFPP)Cl with Mg-Al LDH in the dark, is reduced to $Fe^{II}$(TPFPP) under visible light irradiation. It was confirmed that the Soret band of $Fe^{II}$(TPFPP) was diminished in the presence of $O_2$ under visible light irradiation, indicating that $O_2$ is activated by $Fe^{II}$(TPFPP) not in the dark but under visible light, and the active oxygen species decomposes $Fe^{II}$(TPFPP) (autolysis), as shown in Figures 9(a) and (b). On the other hand, Figure 9(c) shows that a substrate such as cyclohexene inhibits the decrease in the Soret band of $Fe^{II}$(TPFPP) because epoxidation proceeds in

preference to autolysis. It is widely recognized that an Fe-porphyrin complex such as P-450 activates molecular $O_2$, resulting in the formation of a high-valent Fe-oxoporphyrin complex which could be used for the epoxidation of alkenes.[18] Currently, it is not clear whether such a high-valent Fe-oxoporphyrin complex is generated in our photocatalytic system. It is concluded, however, that $Fe^{II}$(TPFPP), which is converted from $Fe^{III}$(TPFPP)Cl via $Fe^{III}$(TPFPP)OH in the presence of Mg-Al LDH under visible light irradiation, acts as a photoactive species in our system, and also plays a major role in generating active oxygen species that trigger the epoxidation of cyclohexene.

## Conclusion

Solid base Mg-Al LDH enhances the conversion of cyclohexene and the selectivity for 1,2-epoxycyclohexane in the photocatalytic aerobic epoxidation of cyclohexene in the presence of $Fe^{III}$(TPFPP)Cl under visible light irradiation. The experimental results clarified that the epoxidation proceeds only when both $Fe^{III}$(TPFPP)Cl and Mg-Al LDH coexist in chloroform in the presence of $O_2$ under visible light irradiation. The OH group of Mg-Al LDH was exchanged with the axial Cl ligand in $Fe^{III}$(TPFPP)Cl. The resulting $Fe^{III}$(TPFPP)OH could be used as a photocatalyst in the presence of Mg-Al LDH. The redox reaction between Fe(III) and Fe(II) takes place under visible light irradiation. $O_2$ is activated by $Fe^{II}$(TPFPP) under irradiation with visible light, and active oxygen species are generated which could be used for the epoxidation of cyclohexene. The homogeneous–heterogeneous $Fe^{III}$(TPFPP)Cl/Mg-Al LDH photocatalytic system effectively promotes the visible-light induced aerobic epoxidation of cyclohexene.

## Experimental Section

$Fe^{III}$(TPFPP)Cl was purchased from Sigma-Aldrich Co. Mg-Al LDH was fabricated by the following coprecipitation method. An aqueous solution containing $Mg(NO_3)_2$ and $Al(NO_3)_3$ was slowly added to aqueous NaOH at room temperature while the pH was kept at 10.0. The resulting suspension was filtered after aging for 12 h at 333 K. The filtrate was washed with distilled water and dried at 378 K for 12 h in an oven. Prior to use, cyclohexene was distilled to remove water and impurities and was subsequently passed through an alumina column to remove any peroxides. Chloroform was used as received. The photocatalytic reaction was carried out in a closed batch system using a Pyrex glass with a flat glass ceiling window for illumination and a rubber balloon to maintain atmospheric $O_2$ pressure. The synthesized Mg-Al LDH (100 mg) was dispersed in a chloroform solution (4 mL) of $Fe^{III}$(TPFPP)Cl ($5.0 \times 10^{-2}$ mM) and cyclohexene (12.5 mM). The liquid suspension was first sparged with $O_2$ for 5 min and then irradiated with a 200 W Hg-Xe lamp (San-Ei Electric Co., Ltd., UVF-204S Type C) equipped with fiber optics, a collective lens, a mirror, and a L-42 cutoff filter ($\lambda > 400$ nm). To determine amount of $CO_2$ evolved, the reaction was carried out in a conventional closed circulating system equipped with online thermal conductivity detector-gas chromatography (TCD-GC) using a GC-8A chromatograph (Shimadzu Corp.). For action spectrum measurements, a JASCO monochromatic light device equipped with a Bunko-Keiki Co., Ltd. CT-10T monochromator and a Ushio SO-X500L 500 W Xe lamp was used. The organic products were analyzed with a Shimadzu Corp. gas chromatograph (GC-2014) using flame-ionization detection (FID) and a GC-mass spectrometer (Shimadzu, GCMS-2010). UV-vis absorption spectra were obtained by a JASCO Corp. V-670 spectrometer. Spectralon®, supplied by Labsphere Inc., was used as a standard reflection sample.

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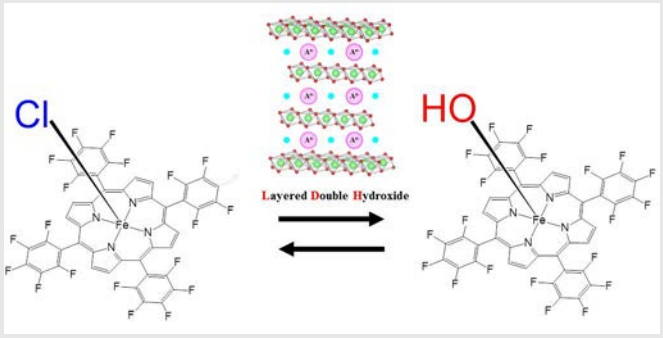


The OH groups in the Mg-Al layered double hydroxide (LDH) exchanged with the axial Cl ligands in $Fe^{III}$(TPFPP)Cl to afford $Fe^{III}$(TPFPP)OH, which functioned photocatalytically in the presence of Mg-Al LDH for the aerobic epoxidation of cyclohexene, but was inactive in its absence.

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**Photoactivation of Molecular Oxygen by an Iron(III) Porphyrin with Mg-Al Layered Double Hydroxide for Aerobic Epoxidation of Cyclohexene**

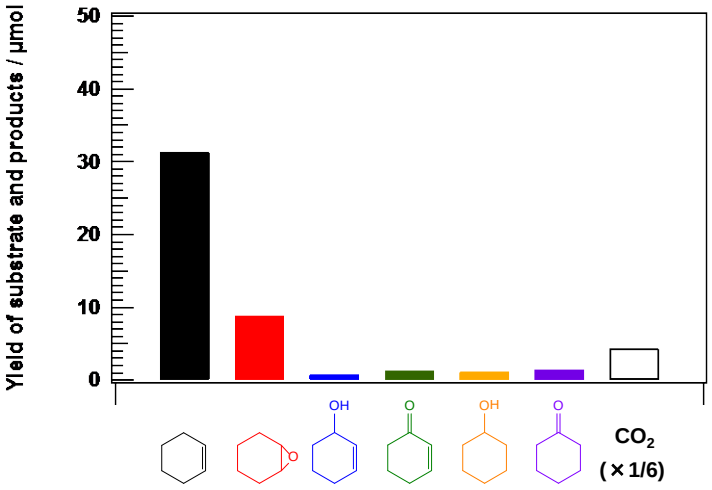


**Figure S1.** Yields of oxidation products and CO2 for the photocatalytic aerobic oxidation of cyclohexene in the presence of $Fe^{III}$(TPFPP)Cl and Mg-Al LDH after 8 h photoirradiation: : cyclohexene (black), 1,2-epoxycyclohexane (red), 2-cyclohexen-1-ol (blue), 2-cyclohexen-1-one (green), cyclohexanol (yellow), cyclohexanone (purple), and CO2 (white). Conditions: $Fe^{III}$(TPFPP)Cl: $5.0 \times 10^{-2}$ mM; cyclohexene: 12.5 mM; Mg-Al LDH: 100 mg; solvent: chloroform; volume: 4 mL.

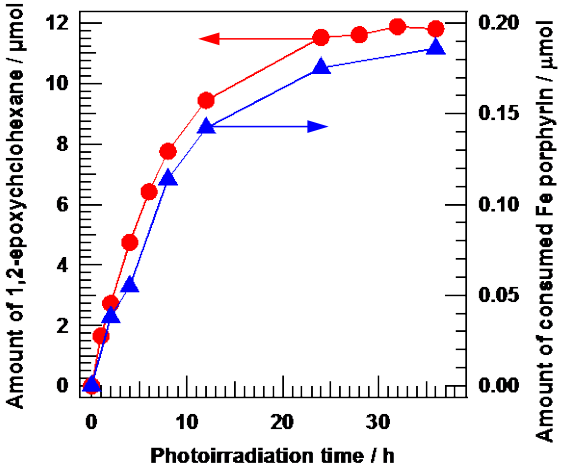


**Figure S2.** Time courses of the evolution of 1,2-epoxycyclohexane and amount of consumed $Fe^{III}$(TPFPP)Cl during the reaction. Conditions: $Fe^{III}$(TPFPP)Cl: $5.0 \times 10^{-2}$ mM; cyclohexene: 12.5 mM; Mg-Al LDH: 100 mg; solvent: chloroform; volume: 4 mL.

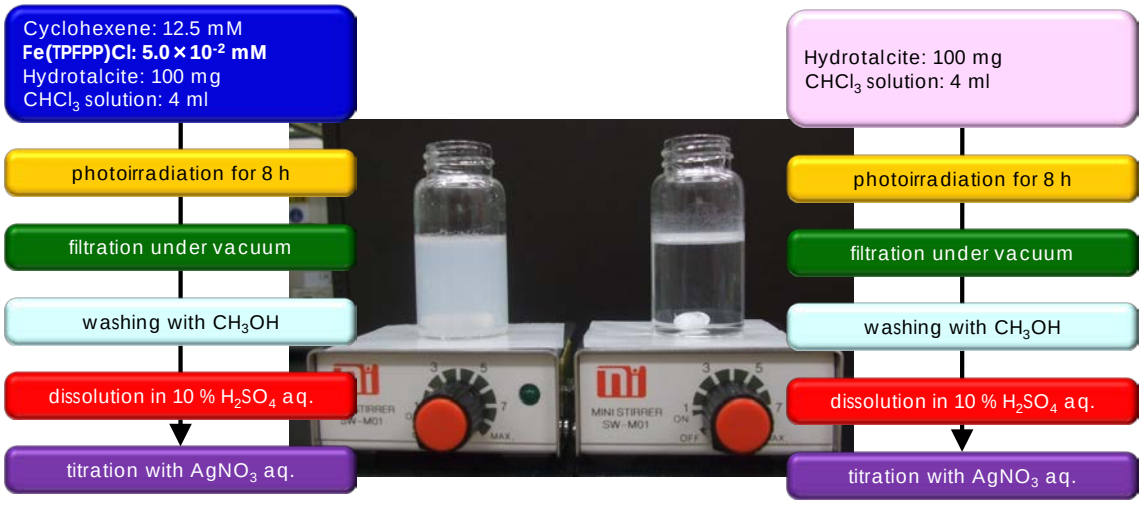


**Figure S3.** Solutions of Mg-Al LDH after photocatalytic reaction, filtration, washing with $CH_3OH$, dissolution with an aqueous $H_2SO_4$ and titration with an aqueous $AgNO_3$: (right) with or (left) without $Fe^{III}$(TPFPP)Cl

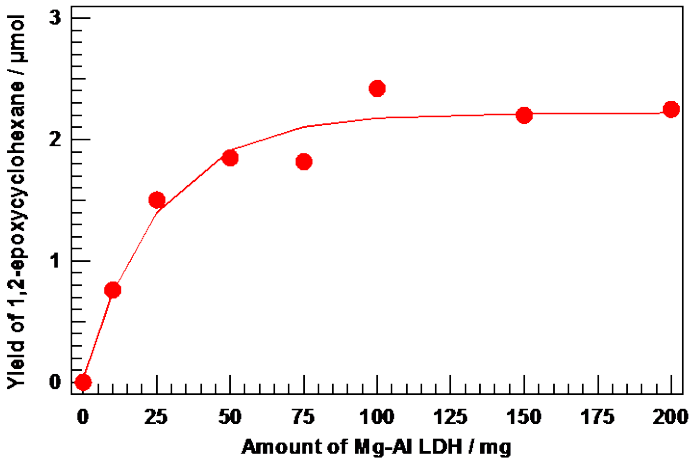


**Figure S4.** Dependence of formation rate of 1,2-epoxycyclohexane on amount of Mg-Al LDH introduced for the aerobic epoxidation of cyclohexene.

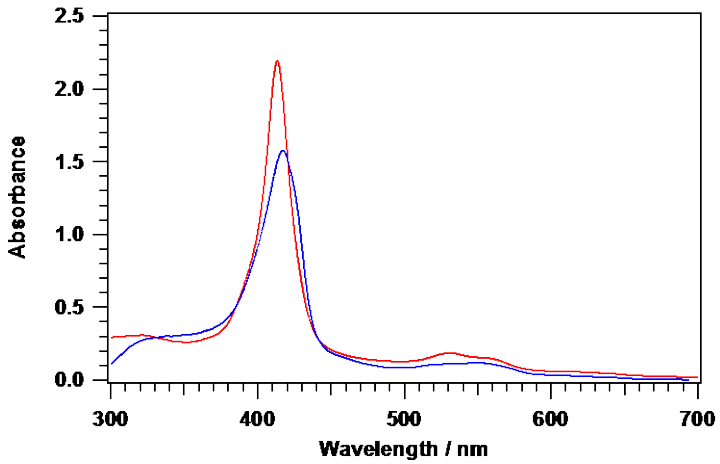


**Figure S5.** UV-vis absorption spectra of $Fe^{III}$(TPFPP)Cl in the presence of Mg-Al LDH after photoirradiation (red line), and after introduction of $Na_2S_2O_4$ as a reductant (blue line).